EVALUATION OF CHLOROPICRIN AS A WARNING AGENT AND EMPLOYEE EXPOSURE OF METHYL BROMIDE AND CHLOROPICRIN DURING STRUCTURAL FUMIGATION*

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This presentation covers a portion of a study we conducted to determine the fate, that is, what happens to the airborne levels of methyl bromide and chloropicrin inside a structure during a typical fumigation. A structural fumigation is where an entire building is covered by a heavy gas-impermeable tarpaulin, the fumigant is introduced and the structure remains under these conditions for 24 to 48 hours. Our study began following a request by a large urban county in California. They had observed that chloropicrin, the warning agent, does not seem to always deter persons from entering a structure undergoing this type of treatment. This unauthorized entry into a lethal atmosphere of methyl bromide has resulted in several fatalities. Because of the fatalities, and resulting questions about the effectiveness of the warning agent with time, we designed a study to find what is happening to this fumigant and the warning agent during these fumigations.

Methyl bromide is commonly used as a fumigant in structural pest control. Each year over a million pounds are used to fumigant thousands of structures in California. Fumigation is an effective method of controlling wood-destroying insects. Major advantages of fumigation compared to other treatments include speed - fumigation is often the quickest method of

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control. Another advantage is effectiveness - the fumigant, as a gas, can reach into places other pesticides cannot. Drawbacks include substantial labor requirements necessary to prepare the structure for this type of treatment, a high degree of technical skill to obtain an effective treatment and maintain a safe working atmosphere and the hazard of working with a toxic pesticide in a gas form.

Methyl bromide is a colorless gas with practically no odor and causes no immediate irritation of the nose or respiratory tract, even at severely poisonous concentrations. Exposure to IDLH concentrations, can produce rapid narcosis and death from respiratory failure. The IDLH concentration for methyl bromide is 2000 ppm. Since this gas lacks any type of warning property, chloropicrin is used to provide some indication that the fumigant is present. Chloropicrin, or tricloronitromethane, is an oily liquid at room temperature. This tear gas like chemical can be added separately or a fumigant product that contains the chloropicrin in the formulation can be used. In addition to this warning agent, elaborate safety procedures are used to warn of the hazard. All doors are locked to prevent entry and the structure is posted with signs advising of the hazard. Despite all the care and precautions, over the last ten years, several fatalities have occurred during this type of treatment. In several cases, it appears the victims were burglarizing residences. In other instances, the victims appeared to have been seeking shelter, or were under the influence of drugs or alcohol.

Many questions were posed by these fatalities, such as - how is it that a person could enter into a lethal atmosphere - was there insufficient warning agent present to deter entry? - does the chloropicrin dissipate with time? - does the use of alcohol or drugs dull the senses to the point that a victim was not warned? - should more chloropicrin be required - etc. Certainly, one of the major questions was: is chloropicrin always present in concentrations high enough to be an effective warning agent? Our task, then, was to obtain some measurements of the atmosphere during typical fumigations with this fumigant and the warning agent and to follow the concentration of these materials with time.

For this study, we devised a method to monitor the airborne concentrations of the two gases inside a tarpaulined structure undergoing fumigation. We wanted to measure the concentrations of these gasses simultaneously and continually. This proved to be no easy task. In a typical fumigation, methyl bromide is applied at a label rate from one and a half to three pounds per 1000 cubic feet of structure volume. This should result in a methyl bromide concentration of approximately 6,000 to 12,000 ppm inside the structure. The chloropicrin application rate, if introduced as a separate step, is one ounce per 10,000 to 15,000 cubic feet of structure volume. If formulated into a fumigant product, it is present in at least one quarter to one half of one percent. Both methods of adding the warning agent, should result in a concentration of 15 to 30 ppm of chloropicrin inside the structure. We found it was possible to use Miran infrared gas analyzers to measure the individual concentrations of the two fumigant gases. By carefully examining the infrared spectra of each of these gases, we found a characteristic absorbance band unique to each gas and that did not appear in the spectrum of the other gas. We then tuned one instrument to constantly follow the selected absorption band of methyl bromide and the other instrument was tuned to follow the selected band for chloropicrin. By dedicating an instrument to look at each gas, we were able to monitor the concentration of both gases at the same time. Methyl bromide was relatively easy to measure, because of the high concentration expected within the structure and the relatively small interference expected from the low concentration of the chloropicrin. Chloropicrin was much more difficult to measure because we were trying to look at a low concentration of this gas, less that 30 ppm, in the presence of another gas at much greater concentration, up to or exceeding 12,000 ppm.

For calibration of this instrumentation, methyl bromide concentrations were measured by dedicating one analyzer to respond to a characteristic absorbance band at 7.6 microns in the infrared spectrum. Because of the high concentration expected, the variable pathlength was set to the shortest possible length, four meters. In a similar fashion, another gas analyzer was dedicated to measure chloropicrin. This gas was quantitated at 11.5 microns, a place in the infrared spectrum of chloropicrin where this gas could be detected in the presence of methyl bromide at much greater concentrations. For chloropicrin, the variable pathlength cell was set to a maximum of 21 meters.

After we found it was possible to monitor both gases, we installed our analyzers in a van and began gathering actual field data. The field sampling procedure consisted of several steps: prior to the tarping a structure, we installed a 1/2 inch O.D. polypropylene hose into the structure. The inlet of this hose was positioned at a height of about six feet above the floor in the center of, typically, the living room. The hose was directed out of the building and through our disconnection valves and then into our sampling van. In the van, the hose was connected to one of the analyzers which was connected in series to the other analyzer. An air pump was connected to the downstream side of this sampling train and with this arrangement air could be drawn from inside the structure as the fumigation proceeded. The exhaust side of the air sampling pump was directed back inside the structure. With this sampling system, air from inside the structure undergoing fumigation was constantly withdrawn, run through the instruments in our sampling van where the actual measurements were obtained and then directed back into the structure. Air was moved through this sampling system at a rate of 25 liters per minute. By locating all measuring instruments upstream of the air pump, almost all of the system was below atmospheric pressure. This was an important safety consideration for protection of our staff members working on this project, since any leak in the system would be inward. The sampling hoses were equipped with large ball valves between the structure and our sampling van, permitting us to disconnect the monitoring train from the structure, if desired. The inlet line was also equipped with a two-way valve that enabled us to periodically admit clean outside air to rezero the instruments or flush out the system prior to disconnecting. With this arrangement, we conducted seven monitorings of methyl bromide structural fumigations. We tried to arrive at a structure just prior to the arrival of the fumigation crew. This allowed time to install our inlet and exhaust lines, find an appropriate position for our sampling van, a source of electrical power and time for warm-up of our instruments. The fumigation crew would arrive and cover the structure with the tarpaulins. Our monitoring typically began shortly before the introduction of the fumigant. The concentration of the two gases was monitored continually, constrained only by limits of available staff and considerations of personal safety during late night and early morning hours.

At this point, I would like to use a few slides to illustrate some aspects of this study. This slide (#1) is a diagram of the physical layout of the typical fumigation and shows how our equipment was connected to the structure. Installation of all our sampling equipment in a van allowed us to be highly mobile and we could easily get from site to site. With all the equipment already plumbed and wired together, we could quickly be up and running at each new site. Use of the large ball valves in line from the structure to the sampling van allowed use to disconnect and move the van away from the site at night, or at least flush out the lines and lock up the equipment when the site was unattended.

This slide (#2) is of one of the actual sites, shows how a building appears when tarpaulined and under fumigation. The tarpaulins are draped over the structure. The edges are rolled together and clamped at regular intervals with steel clothespins. The bottom is sealed against the ground with long canvas tubes filled with sand, called sand snakes. This slide shows the location of our sampling van containing the equipment. With the use of long sampling lines, we could position the van on the street, near the structure but far enough away to be safe and to not interfere with the work of the fumigation crew.

This slide (#3) is an interior view of the equipment in our sampling van. You can see the two gas analyzers. Each analyzer was connected to a strip chart recorder to give a permanent record of the monitoring. During the latter portion of this study we obtained two portable gas chromatographs. One of these we used to get a second independent measurement method for the methyl bromide and one we used to get a second independent measurement of the chloropicrin concentrations.

This slide (#4) is a graph showing the results of one of the fumigations. The scale of the abscissa on the left is ppm of methyl bromide, up to 15,000 ppm. The solid line on the graph is the corresponding methyl bromide concentration. The ordinate on the bottom is time in hours. The scale is from the introduction of the fumigant to 40 plus hours. Chloropicrin concentrations are shown by the dotted lines and the scale to 30 ppm is on the abscissa on the right side of the graph. The results of this site are typical of the results obtained at all the other sites. The concentrations of the two gases, after a time of equilibration within the structure, appear to mirror each other with time. From these results we concluded that the chloropicrin is not dissipating at a rate different than that of methyl bromide. For this site, after 40 plus hours there is still over five ppm inside the structure. The ACGIH TLV and the OSHA PEL are both 0.1 ppm for chloropicrin. Eye irritation is present usually around 0.3 ppm. Most people can smell the characteristic odor at about one ppm. Data from World War I reports that a four ppm exposure for a few seconds "rendered a man unfit for combat."

This slide (#5) is a graph of the results from monitoring at two other sites. At both of these sites the fumigation lasted only about 24 hours. In site two, the fumigant and warning agent was introduced in the sub-floor area and the results show that it took some time for the fumigant to equilibrate and reach a maximum air concentration. This fumigation and the one at site number one, that was shown on the previous slide, were conducted by companies that used tarpaulins in very good condition and appeared to take greater care in structure preparation. At this site, chloropicrin concentrations never exceeded 5 ppm but never fell below 2 ppm. At site three, high concentrations were observed initially, followed by a continual dissipation until at the end of 24 hours little of either gas remained. The company that conducted this fumigation used tarpaulins that were not in good repair, did not take the same amount of care in preparing the structure as did the other companies, and the resulting curve is not unexpected.

An additional aspect of this work involved determinations of worker exposure to these fumigants. This slide (6) shows some of the workers removing the tarpaulins. Tarpaulin removal and house clearance procedures were found to be the phases of fumigation operations that can pose the most exposure potential to the fumigation workers. The concentrations of methyl bromide and chloropicrin were measured with personal breathing zone air samples. Methyl bromide was trapped on charcoal tubes and chloropicrin was collected on XAD-4 porous polymer tubes. Results of this sampling show that the initial operations involved in the untarping can result in exposure above occupational guidelines. This sampling also showed that chloropicrin is not a reliable warning agent for exposure to methyl bromide during this phase of the fumigation when the concern is for occupational exposure values. An irony of sorts is the observation that the fumigation companies that have the best equipment, spend the most time on preparation of the structure for treatment, and, essentially, provide the customer with the best job are the companies with workers potentially exposed to the most fumigant during the untarping phase. This is due to a greater concentration of the fumigant remaining inside when the crew arrives to perform the untarping.

In conclusion, we were able to offer the following observations from this work: first, added according to label rates or incorporated into the fumigant product by the manufacturer, the present amount of chloropicrin appears sufficient to deter entry in structures under normal conditions. We have shown that the two gases do not act independently, but instead, dissipate at comparable rates. Second, instead of requiring that more warning agent be added, we suggested a closer look at fumigation work practices, such as the use of only new or well maintained tarpaulins, tightly rolling seams, thoroughly wetting of the soil around the perimeter and the liberal use of clamps and sand snakes. Improving these work practices will maintain a sufficient concentration of the warning agent to deter entry. With regard to worker exposure, it appears that the workplace is not well controlled during the untarping phase. We have suggested that further work be conducted to investigate improved work practices to reduce the level of the fumigant in the structure prior to removal of the tarpaulins.